A Comparison of On-Site and Elevated Temperature Cure of an FRP Strengthening Adhesive

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SUMMARY
This paper examines the effect of cure temperature and humidity upon the glass transition response of a typical ambient-cure epoxy adhesive. The adhesive was cured at two different temperatures (24°C and 50°C) and two extremes of humidity (dry and saturated), for up to 28 days. Its glass transition response was determined using dynamic mechanical analysis (DMA). This fundamental data will be of use to designers and researchers studying the warm temperature response of FRP bonded strengthening and adhesive joints.

The results demonstrate that on site (at 24°C) the adhesive does not achieve full chemical cure, and consequently the adhesive properties used during design (such as the data sheet values) should be based on similar cure conditions. Furthermore, curing the adhesive at elevated temperature to obtain a quick adhesive test result for quality assurance purposes is not necessarily a safe or representative assessment of the long-term properties of the on-site adhesive.

1. INTRODUCTION

The ambient-cure epoxy adhesives used in FRP strengthening undergo a glass to rubbery transition characterised by a glass transition temperature (T_g) typically in the range 60 to 82°C [1]. The adhesive loses strength and stiffness, but gains deformation capacity and viscosity through the glass transition, a process that starts at temperatures below T_g [2]. Prior work by a number of researchers has demonstrated how the glass transition behaviour of bonding adhesives can be important at the service temperatures typically experienced by FRP-strengthened concrete [3,4], FRP-strengthened steel [5,6], and due to creep deformation of the adhesive [7]. Consequently, design must ensure that the adhesive has an adequately high T_g for the in-service conditions that it will experience. Current design guidance typically requires that T_g is 15°C higher than the maximum design service temperature [1,8].

The glass transition temperature (and other properties) of an adhesive depends upon (a) the *degree of chemical cure* (the proportion of potential cross-links that have been formed between polymer chains) and (b) the physical configuration of the polymer chains within the adhesive (*physical ageing*) [9,10]. These in turn depend upon the age of the adhesive, and the temperature and humidity environment to which it has been subjected.

The adhesive in a strengthening scheme may experience temperatures in the region of e.g. 23°C, and consequently might *never* achieve full chemical cure [9,11] (as discussed in greater detail below). The value of T_g quoted on a manufacturer's data sheet, however, might be cured under different conditions to those on-site. The ASTM C881-02 *Standard Specification for Epoxy-Resin-Base Bonding Systems*

for Concrete [12] defines a cure temperature of 23±1°C for characterisation tests on a load-bearing epoxy to be used above 15°C. Data sheets of epoxies sold for FRP strengthening can be found that specify a similar cure environment to ASTM C881; however, other products can be found whose data sheet properties are based upon cure at temperatures substantially above those ever experienced on site (e.g. 60°C for 3 days). Elevated temperature curing of test samples to achieve 'full cure' is founded upon the assumption that the on-site adhesive will also eventually achieve 'full cure', although over a longer time frame. This assumption, however, has not been supported by detailed research work.

Furthermore, *quality control samples* are required to demonstrate that the on-site adhesive has achieved the properties specified by the designer, and these are subjected to a third cure environment that might be different again to the on-site conditions or the data sheet cure conditions. Current practice for the cure of quality control specimens varies; the samples might be cured on-site (or under similar environmental conditions to the on-site works). It is also common, however, to carry out elevated temperature curing to obtain test results quickly, to enable rapid handover and re-opening of a strengthened structure.

This paper reports test data on the effect of cure temperature, humidity, and time upon the glass transition response of a typical FRP bonding adhesive. The data:

- demonstrates the impact of curing conditions upon T_g in a controlled environment;
- provides much-needed data on the glass transition that is required by designers; and
- helps to establish whether adhesive cured under laboratory conditions for data sheet or quality control purposes (e.g. at elevated temperature and/or humidity) is representative of adhesive cured on site.

2. THE ADHESIVE GLASS TRANSITION

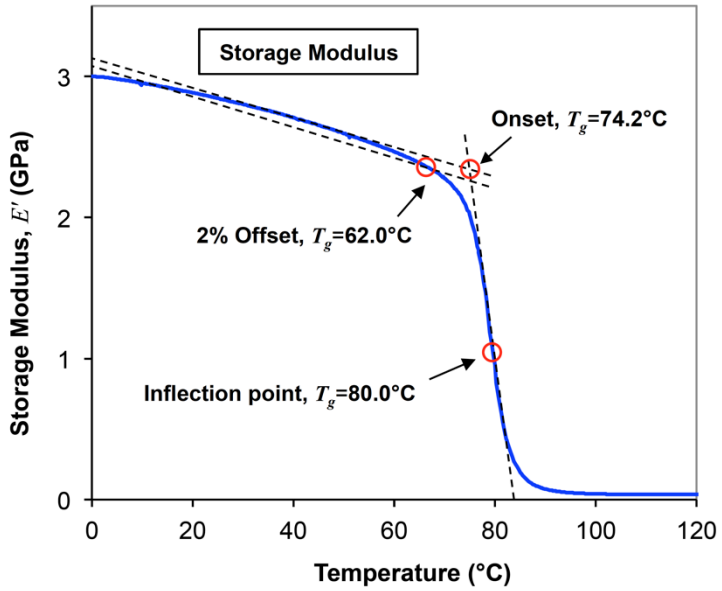
2.1 Characterising the Glass Transition

The design of bonded FRP strengthening is based upon the specified mechanical properties of the adhesive, including the adhesive stiffness. Figure 1 illustrates the change in stiffness of a typical epoxy adhesive through its glass transition. This plot was obtained by the authors as part of the present work using *Dynamic Mechanical Analysis* (DMA), which is the most relevant test method for determining the maximum allowable service temperature for FRP strengthening, because it is a direct measure of the mechanical performance of the adhesive [11].

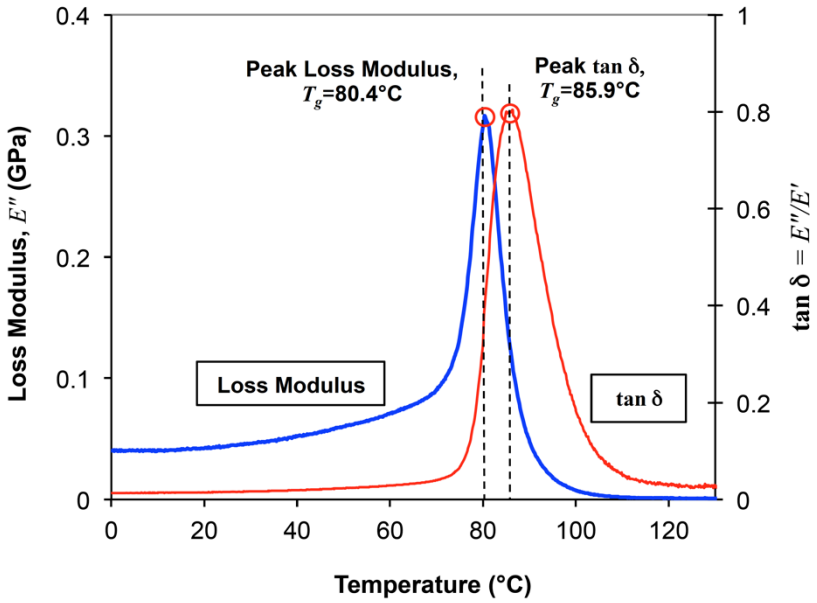
Figure 1 plots the change in storage (elastic) modulus of the adhesive (E'), loss (viscous) modulus (E''), and tan δ with temperature. tan δ is the ratio between the loss modulus and the storage modulus ($\tan \delta = E''/E'$), where δ indicates the phase angle between the cyclic stress and strain [13]. Although the glass transition takes place over a range of temperatures, it is usually quoted as a single value of T_g. There are, however, numerous definitions for T_g, illustrated in Figure 1:

- T_g onset, which is defined by the intersection of a tangent to the storage modulus curve below the transition with a second tangent during transition [14,15];
- T_g 2% offset, the temperature at which the storage modulus has dropped by 2% compared to a tangent to the storage modulus below transition [11];
- the point of inflection in the storage modulus curve [14];
- the peak in the loss modulus curve [14,15]; or
- the peak in the tan δ curve [14,15].

The onset and 2% offset definitions give low values of T_g that appear most suited to defining allowable service temperatures. However, they are sensitive to how the tangent lines are drawn [16], and different values are obtained if a logarithmic scale is used to plot the storage modulus (which is frequent practice). The point of inflection and peak in the tan δ curve are more easily identified and more consistent between tests, although it must be noted that they give high values of T_g [16].



a) Storage modulus response.



b) Loss Modulus and tan δ response.

Figure 1: A typical glass transition response showing the various different definitions of T_g. (Data obtained during the test programme described below; cured for 28 days at 50ºC and 0%RH).

A second method for characterising the glass transition of an adhesive is Differential Scanning Calorimetry (DSC). DSC measures the heat required to raise the temperature of the adhesive, and consequently the glass transition appears as a change in enthalpy. DSC is a direct assessment of the degree of chemical cure of the adhesive (the proportion of the possible crosslinks that have been formed between polymer chains), rather than of the adhesive's mechanical properties [16].

Another method for characterising the thermal response of an adhesive is its Heat Distortion Temperature (HDT) or Deflection Temperature Under Load (DTUL). This determines the temperature that 2% strain is reached in a small beam of adhesive under a specific load and heating rate. Whilst HDT is a pragmatic quality assurance test method, it does not directly characterise the glass transition [16] and it is not clear how HDT relates to the detailed design of an adhesive joint.

2.2 The Effect of Chemical Cure and Physical Ageing upon T_g

The degree of chemical cure describes the number of cross-links formed within the adhesive. A greater degree of chemical cure results in less mobility between the polymer chains and hence an increase in the T_g of an adhesive [11]. The degree of chemical cure that is achieved in the adhesive depends upon both temperature and relative humidity. For the temperatures typically experienced by a strengthening scheme, cross-link formation will finish after around 7 days [9]. Whilst a higher degree of cure could be achieved by raising the temperature above the current T_g of the adhesive, such temperatures are not generally reached on site and deliberate elevated temperature cure is usually impractical and uneconomic.

A second process, however, can lead to increases in T_g for adhesive that remains below its current value of T_g. *Physical ageing* describes reconfiguration of the polymer chains relative to one another, but with no increase in the number of covalent cross-links [9,10]. Reconfiguration of the polymer chains leads to improved adhesive properties (including T_g) due to (e.g.) stronger secondary Van der Waals bonds; the details of the various physical ageing processes are described elsewhere [10].

Hülder [11] used a combination of DSC, DMA, stress-strain, and creep tests to examine the effect of 8°C and 23°C cure upon a commercial ambient-cure epoxy (similar to the one studied in the current work). They demonstrated that the mechanical properties of an adhesive are significantly affected by curing at temperatures below T_g and recommended the use of T_g 2% offset to determine the maximum allowable service temperature. They also identified the difficulty of on-site assessment of the degree of cure of adhesive and the problems of providing a representative cure environment for quality control tests. Jaipuriar [9] examined another ambient cure FRP strengthening epoxy, again using a combination of DSC and DMA. They showed that this adhesive reached an 80% degree of cure and T_g of 44°C after 7 days of 22°C cure, and that the degree of chemical cure could only be increased if the temperature was increased to 70°C (i.e. above its glass transition temperature). T_g, however, increased due to physical ageing when the adhesive was kept at temperatures below glass transition. T_g increased towards 52°C over a period of about a year when the sample was held at 22°C (representing on-site conditions), whereas T_g reached 60°C after 10 days when the sample was held at 35°C [9].

3. EXPERIMENTAL METHODOLOGY AND PROGRAMME

The tests described in this paper examine the effect of cure environment on the glass transition response (characterised using DMA). Sikadur 330 epoxy adhesive was studied because it is widely used for CFRP plate bonding and for impregnating carbon strengthening fabrics; the performance of other FRP bonding adhesives is not expected to be substantially qualitatively different.

3.1 Sample Preparation

The adhesive was mixed according to the manufacturer's recommendations, and cast into 1.5×10mm strips. Custom made moulds were used, designed to give good dimension tolerance and to avoid the inclusion of air bubbles within the adhesive during filling. All specimens were left in the moulds for 24 hours under laboratory conditions (24±1°C and 45±5%RH) before being de-moulded and cut into the 25mm lengths required for DMA testing.

3.2 Curing

After removal from the moulds, the samples were cured at either 24±1ºC in the laboratory or 50±1ºC in a drying oven. A desiccant was used to keep half of the samples in a dry environment (close to 0%RH); the other half was cured under distilled water, representing the two extremes of humidity. The samples were tested 3, 7, 14 or 28 days after the specimens were cast (including the initial day at 24ºC prior to de-moulding). Three samples were tested for each cure condition, as summarised in Table 1, which also gives key test results that will be discussed below.

3.3 DMA Testing

A Triton Tritec 2000 DMA machine was used to determine the glass transition responses of the specimens. The liquid nitrogen capability of the machine was used to first cool the specimens to slightly below 0ºC. After the temperature had stabilised, the samples were tested at a heating rate of 2ºC/min and oscillation frequency of 1Hz in a single cantilever configuration. The storage modulus, loss modulus and tan δ responses were obtained and the glass transition temperature was calculated based upon the peak in the tan δ curve.

4. RESULTS AND DISCUSSION

4.1 The Effect of Cure Environment upon Glass Transition Temperature, T_g

Table 1 records the glass transition temperatures obtained (based upon the peak in the tan δ curve) for all of the specimens tested. The averages and standard deviations of the results from the groups of three specimens cured under the same conditions are also given. The same data are plotted in figures 2 and 3.

Table 1: Glass Transition Temperature Results

		Glass Transition Temperature, T_g (°C)			
Curing Temperature	***Curing Humidity***	***3 days***	***7 days***	***14 days***	***28 days***
24°C	Dry	55.3	58.9	61.6	62.6
		55.8	59.0	61.5	63.5
		56.5	58.7	61.5	63.3
	Avg ± SD	*55.9 ± 0.5*	*58.9 ± 0.1*	*61.5 ± 0.0*	*63.1 ± 0.4*
	Saturated	54.0	58.5	56.8	57.5
		56.2	57.2	57.5	57.3
		54.0	57.4	57.2	57.3
	Avg ± SD	*54.7 ± 1.0*	*57.7 ± 0.6*	*57.2 ± 0.3*	*57.4 ± 0.1*
50°C	Dry	79.7	82.8	84.2	84.5
		80.6	83.0	84.7	84.7
		80.1	83.1	83.4	85.9
	Avg ± SD	*80.1 ± 0.4*	*83.0 ± 0.1*	*84.1 ± 0.5*	*85.0 ± 0.6*
	Saturated	67.9	68.8	68.0	68.8
		67.7	69.6	68.4	68.2
		67.8	68.2	68.3	68.9
	Avg ± SD	*67.8 ± 0.1*	*68.9 ± 0.6*	*68.2 ± 0.2*	*68.6 ± 0.3*

Figure 2 shows the variation in T_g with conditioning time for samples cured at 24°C. Under dry conditions, the glass transition temperature rose to a maximum of 63°C after 28 days. Under saturated conditions, however, T_g plateaued at 57°C, and there was no increase in T_g after 7 days. The saturated cure curve is lower than the dry curve at all conditioning times. These results illustrate the significant effect of moisture upon epoxy resin cure. As well as affecting the chemical cure of the early age epoxy, moisture affects the Van der Waals bonds between polymer chains, and (as discussed above), these influence the glass transition temperature and play an important role in physical ageing processes.

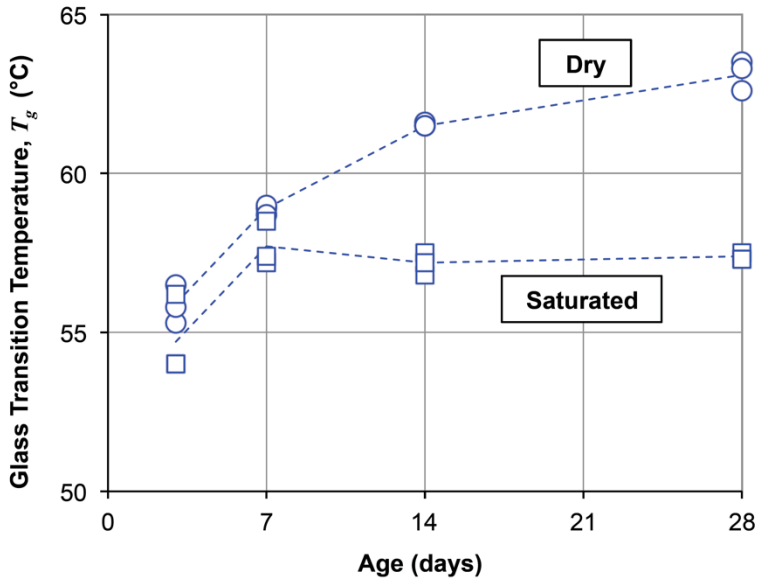


Figure 2: Glass transition temperature variation with conditioning time at 24°C.

Figure 3 plots the variation in T_g with conditioning time for samples cured at 50°C. At this temperature, T_g for the dry specimens rose to a value of 85°C after 28 days. T_g for the saturated samples was substantially lower at 68°C, and did not significantly change from its value after 3 days.

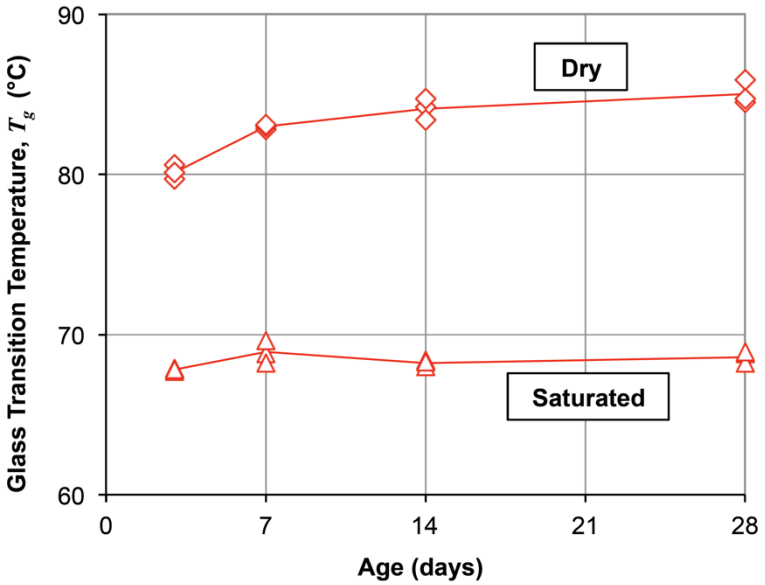


Figure 3: Glass transition temperature variation with conditioning time at 50°C.

The two sets of results are plotted on the same axis in Figure 4. The results demonstrate that dry adhesive cured on-site (where the temperature could be 24°C or substantially lower) achieves a glass transition temperature after 28 days that is 22°C lower than if it was cured in the lab at 50°C. Furthermore, the on-site glass transition temperature after 28 days is 17°C lower than the 3 day 50°C result, showing that elevated temperature cure in the laboratory cannot generally be used to accelerate the cure process such that it represents eventual conditions on-site. As discussed above, if the adhesive remains at 24°C, it may never achieve the same degree of chemical cure as adhesive cured at 50°C, and this is evident from the results shown in Figure 4.

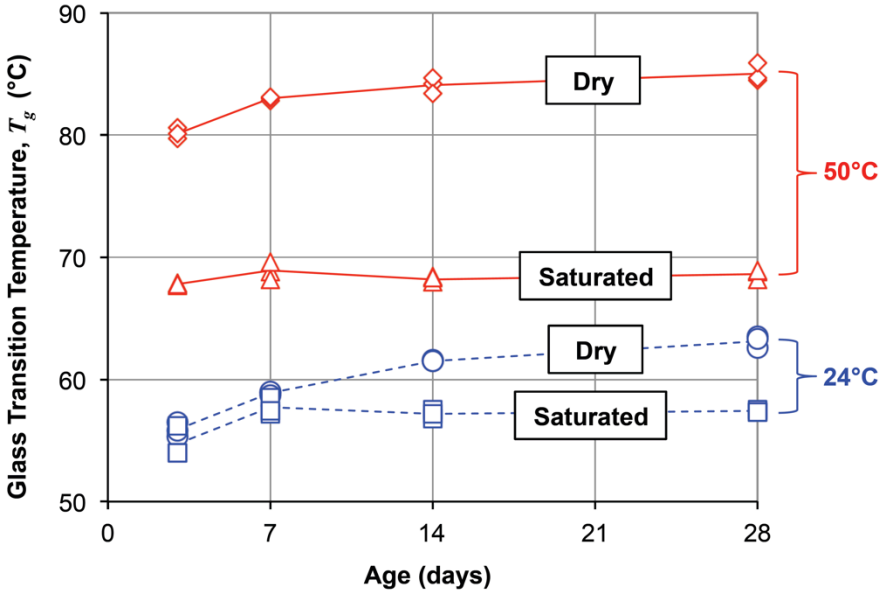


Figure 4: Glass transition temperature variation with conditioning time.

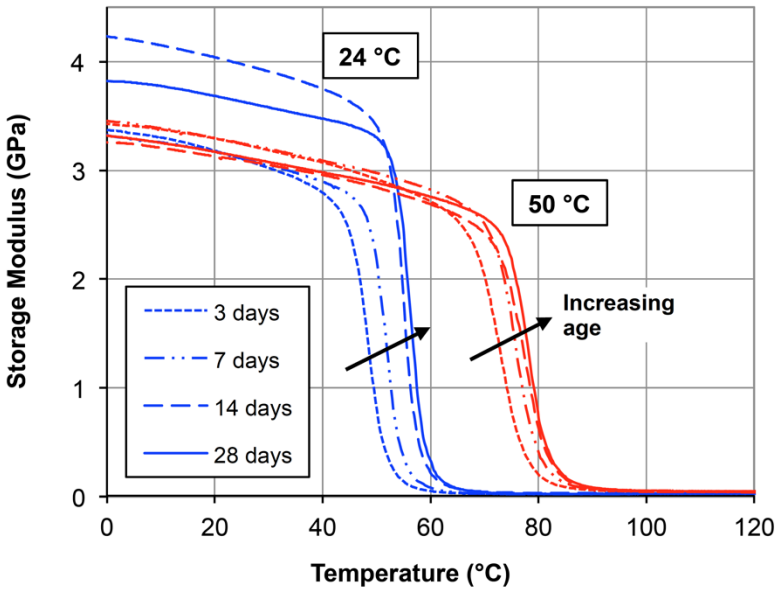
4.2 The Effect of Cure Environment upon Glass Transition Response

The glass transition temperature results reported in the previous section are a useful indication of the effect of cure environment upon the adhesive. The glass transition temperature, however, is only a single point that characterises the glass transition response of the adhesive. The peak in the tan δ response has been chosen here for its ease of identification, but the mechanical properties (stiffness and strength) of the adhesive reduce significantly before this value of T_g is reached. It is thus important to examine the full glass transition response.

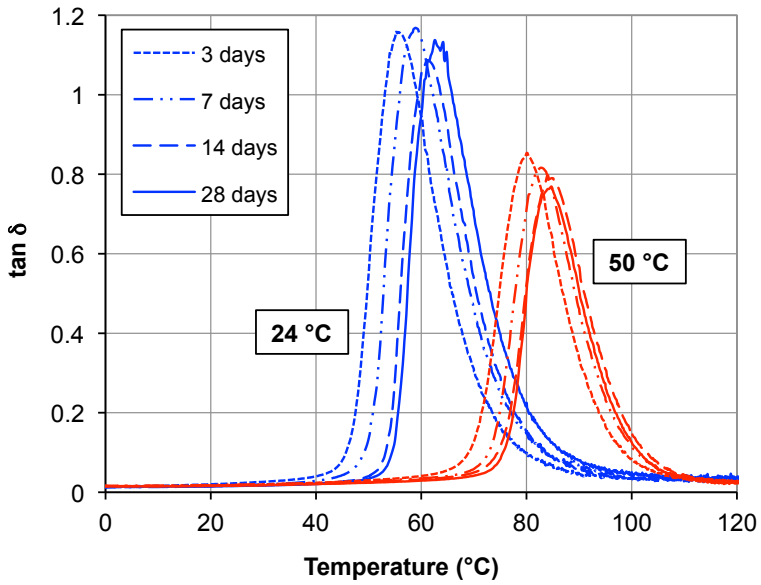
Figure 5 shows the glass transition response for specimens cured under dry conditions, using a representative sample for each conditioning temperature and age. The glass transition response is plotted as the variation in storage modulus with temperature in Figure 5a, and the variation in tan δ in Figure 5b (the peak of which gave the values of T_g reported in Table 1).

The *magnitudes* of the storage modulus curves are not expected to be accurate, due to the length of span, and the clamping arrangements used in the DMA tests (mentioned above). In particular, the 24°C conditioned storage modulus curves give a wide variation in initial modulus (at 0°C), which is thought to be due to slight inaccuracies in the dimensions of these specimens, but are in acceptable agreement to those on the manufacturer's data sheet (3.8GPa after 7 days at 23°C). It is the relative reduction in stiffness that is of interest during DMA testing, and the glass transition temperature is not sensitive to the magnitude of the initial stiffness recorded.

Both the storage modulus and tan δ plots show improvement in the adhesive response with age at both cure temperatures. The storage modulus curves suggest that using the current practice [1,8] of requiring T_g to be 15°C higher than the maximum design service temperature ensures that the adhesive will not reach the sharp drop in performance that accompanies the glass transition; e.g. for 28 days cure at 24°C, (T_g - 15°C) = 48°C. An adhesive at this temperature has 9% less elastic stiffness than at 20°C, but retains the majority of its mechanical performance. As noted above, however, T_g cannot safely be obtained using elevated temperature cure: for 3 days cure at 50°C, (T_g - 15°C) = 75°C, and on-site adhesive has lost essentially all mechanical performance at this temperature.



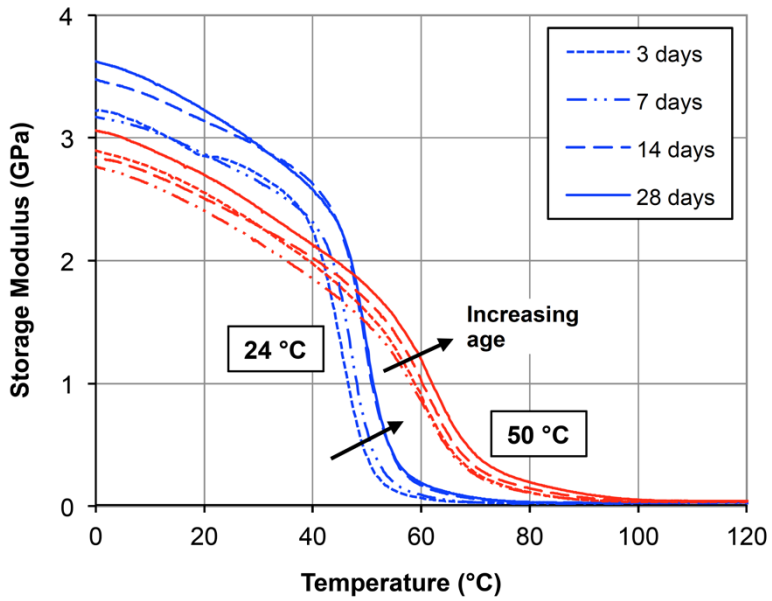
(a) Storage modulus variation with temperature



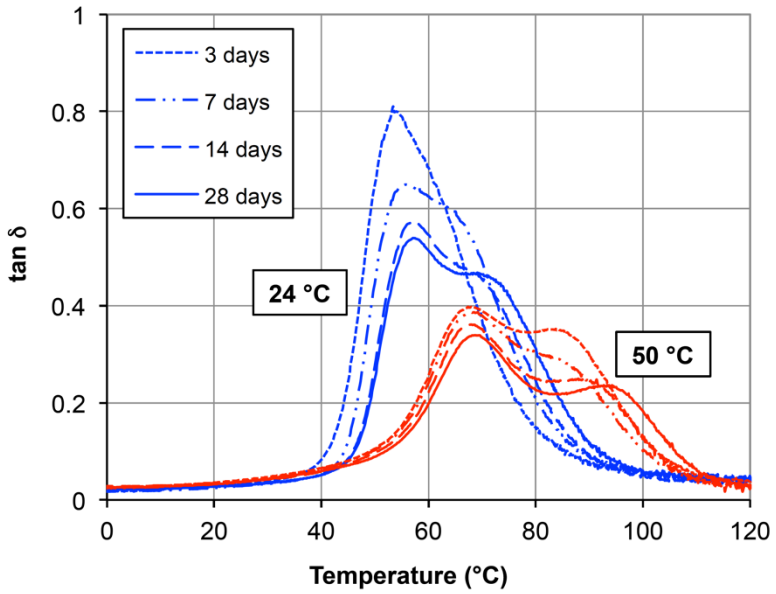
(b) tan δ variation with temperature

Figure 5: Glass transition responses for samples conditioned under dry conditions

Figure 6 plots the storage modulus and tan δ responses for samples cured under saturated conditions. It confirms the substantial effect of moisture upon the adhesive's performance. The degradation in storage modulus at low temperatures is more pronounced than for the dry samples, and there is a less distinct glass transition (apparent as a double peak in tan δ) due to the effect of the water upon the cure kinetics of the adhesive.



(a) Storage modulus variation with temperature



(b) tan δ variation with temperature

Figure 6: Glass transition responses for samples conditioned under saturated conditions.

5. CONCLUSIONS

Data have been presented in this paper that show the effect of curing temperature and humidity upon a typical ambient cure epoxy resin (which is widely used for FRP strengthening purposes). These data include the variation in adhesive stiffness with temperature, which is required by designers and researchers to properly understand the effect of temperature upon the adhesive connection [6]. Data have been presented for both dry and saturated cure that demonstrate the well-known detrimental affect of moisture upon the cure of epoxy adhesive.

Adhesive cured under dry conditions at 24°C (which may be higher than ever achieved on-site) reached a glass transition temperature (T_g) after 28 days of 63°C, 22°C lower than if it had been cured at 50°C. This difference in the T_g of the adhesive may substantially affect an FRP strengthening scheme's ability to carry load at warm temperatures. An on-site cured FRP strengthening scheme

would consequently be expected to fail before one cured at 50°C during a transient heating event (such as warming during an especially hot day, or from the exhaust of a railway locomotive that stops beneath a strengthened bridge).

Furthermore, the 28 day stiffness of adhesive cured at 24°C is 17°C lower than the 3 day stiffness for 50°C cure. Short-term tests on elevated temperature cured specimens cannot be used to predict the long-term performance of the on-site adhesive, because the on-site adhesive may never achieve the same degree of chemical cure. Both the quality control samples and the tests reported on manufacturer's data sheets should be cured under similar conditions to those present on-site.

Further work is underway that will provide additional information upon the elevated temperature response of epoxy adhesives. This will give a more complete data set for design and research.

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